Title: Frontiers in molecular *p*-block chemistry: from structure to reactivity

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Abstract: This year marks the 350th anniversary of the discovery of phosphorus by the alchemist Hennig Brand. It wasn't until more recently though that P was put into the *p*-block. 2019 also marks the 150th anniversary of the preliminary tabular arrangement of the elements into the Periodic System by Mendeleev. Of the 64 elements known in 1869, over a third of them belonged to what ultimately became the *p*-block, and Mendeleev predicted the existence of both gallium and germanium as well. The elements of the *p*-block have a disparate and varied history. Their chemical structure, reactivity, and properties vary widely. Nevertheless, in recent years, a better understanding of trends in *p*-block reactivity, particularly the behavior of those elements not typically found in biological systems, has led to an exciting array of emerging applications, highlighted herein.

One Sentence Summary: This article highlights recent key fundamental and applied studies relating to structure and reactivity which are changing common perceptions of the *p*-block.

Main Text: The Periodic Table now comprises well over 100 elements, each with its own unique chemistry. Among the *p*-block elements, on the right-hand side, the chemistry of carbon, in conjunction with a small number of other elements, has a pre-eminent position in the discipline. The importance of organic chemistry cannot be understated as it defines important aspects of biological chemistry, pharmaceuticals, polymers, and materials science. As a consequence, the exploration of organic chemistry has dominated the efforts of chemists over the past two centuries. During this same time frame, the chemistry of the remaining elements in the *p*-block has garnered much less attention, often with a mere handful of research groups worldwide doing their best to explore and understand the underlying principles which convert a disparate set of observations into a systematic vision of chemical reactivity. This deficiency was further exacerbated by the fact that, in contrast to carbon where the chemistry is dominated by the tetravalent state, many other elements form multiple valencies and oxidation states whose reactivity patterns are each unique. This leaves our understanding of the chemistry of the other *p*-block elements far short of that established for carbon.

The range of non-metals, metalloids, and metals, multiple oxidation states and valencies within the *p*-block provides a tremendous wealth of structures ranging from covalent molecules and polymers to metals, alloys and ionic solids with varied properties. This diversity has both fundamental and practical implications, providing insights for the foundation for life on earth and finding applications in pharmaceuticals, clothing, plastics or electronic devices. At the top of the

p-block, elements typically follow classical bonding models and are the focus of organic chemists where the synthesis, structure, reactivity, and properties of chemical compounds primarily constructed of carbon are studied. Even here there are notable exceptions where boron forms a large family of hydrides where the apparent deficiency in bonding electrons leads to extensive multicenter bonding which contrasts with the classical hydrocarbon counterparts. The heavier *p*-block elements, however, are very different from their lighter counterparts displaying unusual bonding patterns and reactivity. Indeed, the behavior of the heavier *p*-block elements has been said to resemble that of the transition metals.(*1*,2) The diverse and sometimes enigmatic reactivity observed within the *p*-block is often chaotic, inspiring researchers to gain a deeper understanding of structure, bonding, and reactivity thereby acquiring an enhanced appreciation of these dynamic elements. An understanding of the reactivity of these elements and their compounds can have important subsequent ramifications in the applications of the *p*-block elements, whether it be in materials, synthesis or catalysis. It is this latter aspect of *p*-block chemistry that has begun to emerge in the last two decades, generating a renaissance in this field. This review highlights the findings that are, and continue to inspire, the current renewed interest in the chemistry of *p*-block elements in molecular chemistry from fundamental studies to small molecule activation and catalysis. It should be noted that the focus on structure and reactivity presented here, leads to a large area of solid-state and molecular materials chemistry which is not described. This is by no means of any lesser importance but just falls beyond the scope of the current article.

Fundamental studies

Many studies surrounding heavier *p*-block element reactivity have been brought about by variously making comparisons to, or contrasting with, well-established carbon chemistry. Through creating conceptual bridges between inorganic and organic chemistry, a deeper understanding of electronic structure and the ability to predict chemical reactivity can be made. This includes *inter alia* the structure and bonding in cluster compounds, *p*-block polymers, and multiple bonded systems.(*3*,*4*,*5*) Over the past few decades, the isolobal analogy has provided a theoretical foundation for rapid experimental developments in the chemistry of the *p*-block.(*6*) For example, the synthesis of urea in 1828 is often considered the foundation of modern organic chemistry.(*7*) Nonetheless, it was not until recently that a phosphorus-containing urea derivative $H_2PC(=O)NH_2$ was synthesized from the anion $[O{-}C{\equiv}P]^-$ (Fig. 1A).(*8*,*9*) Indeed, one area of focus has been in the synthesis of new *p*-block reagents such as $[O{-}C{\equiv}P]^-$. For example, white phosphorus (P_4) is a common industrial reagent for the synthesis of value-added phosphorus-containing compounds. Yet, the synthesis of these compounds is both energy intensive and hazardous involving the reaction of P_4 with chlorine gas.(*10*) The search for safer, cheaper and more environmentally friendly alternative reagents, has prompted the development of the bis(trichlorosilyl)phosphide anion, $[P(SiCl_3)_2]^-$ (Fig. 1A), which can be used in the synthesis of a variety of phosphorus-containing compounds.(*11*) Other reagents for incorporating *p*-block elements into compounds have included phosphinonitrenes (Fig. 1A). This first isolable non-metallic nitrene derivative was found to transfer a nitrogen atom to isopropyl isonitrile affording a carbodiimide.(*12*)

The strength of multiple bonding is a common theme of organic chemistry and is facilitated by efficient orbital overlap associated with smaller 2*p* orbitals. In these systems, the strength of π-bonding is comparable with σ-bonding. On descending the *p*-block, the more radially expanded nature of the *p*-orbitals leads to a reduced overlap integral and weaker bonds, and σ-bonds become

significantly favored over π-bonds. The isolation of heavier main group compounds containing multiple bonds has therefore been of fundamental interest. These are expected to have much enhanced reactivity (in relation to their carbon analogs) arising from the inherent weakness of these multiple bonds. A common strategy to stabilize these multiply-bonded species is the use of sterically demanding substituents to protect low-valent, reactive main group centers. These bulky groups typically prevent polymerization or oligomerization of monomeric units and preclude attack by nucleophiles or electrophiles.(*3*) Following the first report of the tin analog of an alkene in the 1970's,(*13*) other group 14 alkene derivatives were synthesized including the landmark disilene (Fig. 1B).(*14*) While alkenes adopt a planar geometry, the heavier group 14 analogs $R_2E{=}ER_2$, deviate from planarity reflecting a change in bonding pattern. Such compounds can be considered as dimers of R_2E where the group 14 R_2E unit is amphoteric, possessing both a Lewis basic lone pair and a vacant Lewis acidic orbital. Likewise, the heavier geometrically distorted group 14 derivatives of alkynes, RE≡ER, have also been developed, although more sterically demanding substituents were required.(*3*)

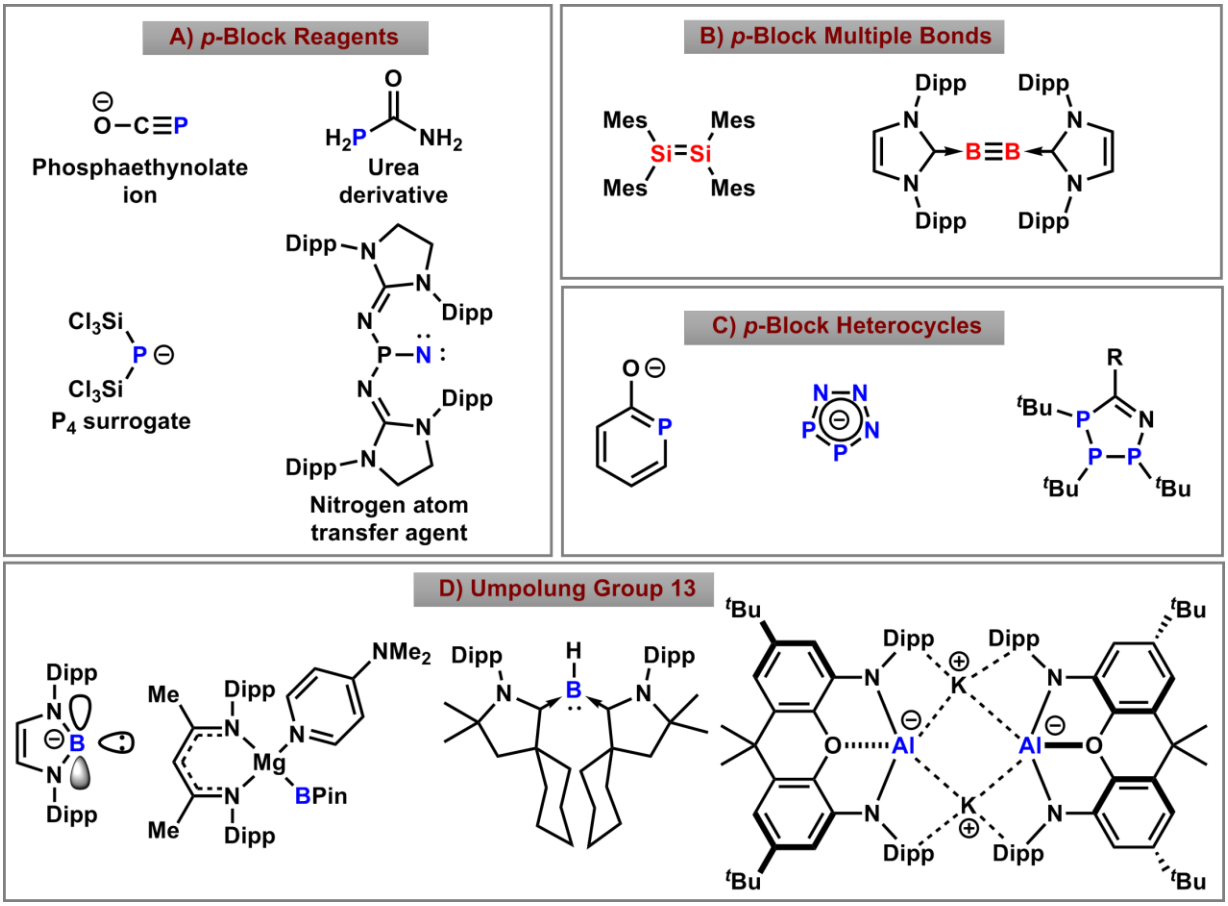

Fig. 1. Fundamental studies. (**A**) Novel *p*-block reagents. (**B**) Multiple bonds. (**C**) Heterocycles. (**D**) Nucleophilic group 13 compounds. Mes = mesityl; Dipp = 2,6-diisopropylphenyl.

A large sample of compounds containing homonuclear and heteronuclear multiple bonds for heavier *p*-block elements ($n > 2$) are now known.(*3*) However, whereas the first row elements

carbon and nitrogen readily form strong triple bonds, boron does not. A recent breakthrough in this area was the stabilization of a boron-boron triple bond. Within the "B≡B" unit, each boron is Lewis acidic and addition of a strong donor such as an N-heterocyclic carbene (NHC) generates a L→B≡B←L compound analogous to an alkyne (Fig. 1B).(*15*) Such an interpretation has been challenged by the proposition that the π-character of the NHC is conjugated with the triple bond to afford an alternative resonance form, $R_2C{=}B{=}B{-}CR_2$.(*16*)

Although aromatic species are ubiquitous in organic chemistry, aromaticity in main group heterocycles has been more controversial. Borazine, $B_3N_3H_6$, is considered aromatic but with much lower aromatic stabilization than the isoelectronic benzene.(*17*) The potentially aromatic nature of many planar heavy *p*-block heterocycles has been discussed, a recent example being the development of the diphosphatriazolate $P_2N_3^-$ heterocyclic anion (Fig. 1C).(*18*) A similar CNP_3 heterocycle was reported more recently, synthesized from the reactions of a cyclotriphosphine (^{t}BuP)$_3$ with nitriles to access 1-aza-2,3,4-triphospholenes (Fig. 1C).(*19*) The 2-phosphaethynolate anion, $[O{-}C{\equiv}P]^-$, described earlier has also been found useful as a potential building block for the synthesis of heterocyclic organophosphorus compounds such as phosphinin-2-olates (Fig. 1C) through stepwise cycloaddition reactions.(*20*) The cycloaddition reactions of this anion can be contrasted with the related cycloaddition chemistry of isolobal, $[S{=}N{=}S]^+$.(*21*)

Another strategy to uncover distinct chemistry involves targeting inverse or umpolung reactivity of *p*-block elements. For example, whereas group 13 elements typically act as Lewis acids, boryl anions can behave both as a base and a nucleophile. For instance, reduction of *N*,*N*'-bis(2,6-diisopropylphenyl)-2-bromo-2,3-dihydro-1H-1,3,2-diazaborole leads to a cyclic boryl anion (Fig. 1D).(*22*) This species, which is isoelectronic with an NHC, exhibits nucleophilic behavior in the reactions with alkyl halides, aldehydes, water, and methyl trifluoromethanesulfonate. Organoboranes incorporating the –BPin (Pin = pinacolate) functionality are widely used intermediates in organic synthesis and in the synthesis of pharmaceuticals, and finding optimal routes to incorporate boron into organic molecules is of paramount importance.(*23*,*24*) Though [BPin] functionalities are traditionally electrophilic, examples of nucleophilic source of the [BPin] moiety are known(*25*) including the recently reported magnesium boryl derivatives (Fig. 1D).(*26*) Another area of interest in group 13 chemistry has been approaches to generate low oxidation state triels. Whereas the inert pair effect makes species such as In^+ stable and Lewis basic/nucleophilic, univalent group 13 elements such as B(I) and Al(I) are rare but are expected to offer significantly different reactivity from their compounds in the more common Lewis acidic/electrophilic +3 oxidation state. For example, nucleophilic boron(I) compounds, which are isoelectronic to amines, can be synthesized by reduction of a CAAC→BBr_3 (CAAC = cyclic (alkyl)(amino)carbene) adduct generating the borylene (H-B:) (Fig. 1D).(*27*) Here the CAACs act as strong π-acceptor ligands to stabilize the lone pair on boron.(*28*) Lewis basicity of the boron lone pair was demonstrated through protonation. As ligands these species could potentially act as better donors than amines or phosphines owing to their higher nucleophilicity. Further down group 13, nucleophilic low oxidation state aluminum species can also be developed, such as the dimethylxanthene-stabilized potassium Al(I) compound (Fig. 1D) which reacts with benzene by C-H oxidative addition.(*29*)

Small molecule activation

The requirement of energetically accessible occupied and unoccupied orbitals for the activation of small molecules was previously thought to limit such reactivity to the *d*-block metals. In 2005, the addition of hydrogen to a main group center was reported: specifically, the germanium alkyne analogue ArGe≡GeAr (Ar = 2,6-$Trip_2$-C_6H_3, Trip = 2,4,6-tri-*iso*-$propyl_3$-C_6H_2) was shown to undergo oxidative addition with H_2 yielding Ar(H)Ge=Ge(H)Ar, $Ar(H)_2Ge$-$Ge(H)_2Ar$ and $Ge(H)_3Ar$.(*30*) Similar studies have subsequently been reported with other low valent group 13 and 14 compounds including aluminium, gallium, and tin (Fig. 2A).(*1*) The activation of dihydrogen in these cases involves synergistic bonding and back-bonding interactions of the frontier orbitals, whereby the σ-orbital of H_2 donates into a low-lying vacant orbital on the *p*-block system and the HOMO of the *p*-block system donates to the H_2 σ*-orbital (Fig. 2B). Analogous activation of dihydrogen at a single carbon site of a CAAC and an acyclic (alkyl)(amino)carbene species was reported in 2007 (Fig. 2A).(*31*) This reactivity results from the much more nucleophilic and electrophilic nature of these carbenes in relation to the archetypical NHCs.(*28*) In contrast to the transition metal oxidative addition of H_2, the carbene behaves as a nucleophile donating into the H-H σ*-orbital prompting hydride delivery to the vacant orbital on the carbon center (Fig. 2B). The unique electronic nature of CAACs also allows them to undergo reversible oxidative addition of C-B bonds(*32*) as well as to activate ammonia,(*28*) a reaction typically not observed with transition metals due to adduct formation.

The underlying principle in chemical reactivity of Lewis acidity and basicity has been known for almost 100 years. Typically, when paired, the Lewis base will donate into the vacant orbital of the Lewis acid to form an adduct. However, in 2006, through the use of sterically demanding groups, unquenched Lewis acidic and basic sites were identified in *p*-$(Mes_2P)C_6F_4(B(C_6F_5)_2)$. This compound was shown to activate hydrogen yielding the phosphonium borate *p*-$(Mes_2PH)C_6F_4(BH(C_6F_5)_2)$ (Fig. 2A).(*33*) Importantly, this compound also releases dihydrogen above 100 ºC regenerating the original phosphine borane. Such reversibility of substrate binding is a key requirement for enabling catalytic turnover (*vide infra*). This finding spawned the field of frustrated Lewis pair (FLP) chemistry.(*34*) For just over a decade, the concept of FLPs has altered the way we think about the reactivity of the *p*-block elements, prompting new reagent design strategies and discovery of ensuing reactivity. Many different FLPs are now known, employing diverse *p*-block bases commonly derived from the group 15 or 16 elements and *p*-block Lewis acids usually based upon the group 13 or cationic group 13, 14, or 15 elements.(*34*) Although rarer, FLPs containing *s*- or *d*-block elements as the Lewis acid or base are also known.(*35*) The mechanism of activation of H_2 by FLPs has been the subject of several computational studies in which theory predicts a trimolecular mechanism involving H_2 and a Lewis acid and Lewis base.(*36*,*37*) The FLP $^tBu_3P/B(C_6F_5)_3$ was calculated to proceed through a two-electron diamagnetic mechanism, whereby the Lewis acid and base approach each other forming a $^tBu_3P\cdots B(C_6F_5)_3$ "encounter complex" in which the two species are 4.2 Å apart. In this species, the Lewis acid and base have their frontier orbitals correctly aligned for dative bond formation, but adduct formation is precluded on the basis of steric hindrance. In this configuration, the system is perfectly set up for synergic interactions with dihydrogen. Inclusion of dihydrogen in the encounter complex results in simultaneous polarization of H_2 through donation of the lone pair of electrons on the Lewis base into the H-H σ*-orbital, and concurrent donation of the electrons in the H-H σ-bond into the boron vacant *p*-orbital (Fig. 2B). This leads to protonation of the phosphine and hydride delivery to the borane. This mechanism, which pertains for many FLP systems, is comparable to that exhibited by bifunctional transition metal complexes(*38*) and is conceptually similar to the synergic interactions described for other main group systems and

transition metal centers. More recently, an alternative single electron transfer (SET) mechanism for FLP activation of dihydrogen has been suggested based on the $Mes_3P/B(C_6F_5)_3$ FLP.(*39*)

Although the activation of dihydrogen by *p*-block systems has garnered much attention, the activation of other small gaseous molecules including acetylene, ethane, CO, CO_2, NO, N_2O, and SO_2 has also been sought.(*40*) These studies have been driven not only by curiosity over which other molecules reactive *p*-block elements can activate, but also in search of new practical systems that can bind, sequester, and potentially transform these molecules. The binding of carbon monoxide by transitions metals *via* synergic σ-bonding and π-back-bonding interactions is a key concept in undergraduate inorganic textbooks. However, mono-adducts and multi-carbonyls $[E](CO)_x$ outside the *d*-block are very uncommon. The borane dicarbonyl complex, $TpB(CO)_2$ (Tp = 2,6-di(2,4,6-triisopropylphenyl)-phenyl) was prepared only recently *via* liberation of a borylene ligand from $[(OC)_5Mo(BTp)]$.(*41*) The bonding in this compound, which is isoelectronic with $(CAAC)_2BH$ described earlier, is reminiscent of that for metals in which there is extensive back-bonding from the filled *p*-orbital on boron into the C≡O π*-orbital.(*41*)

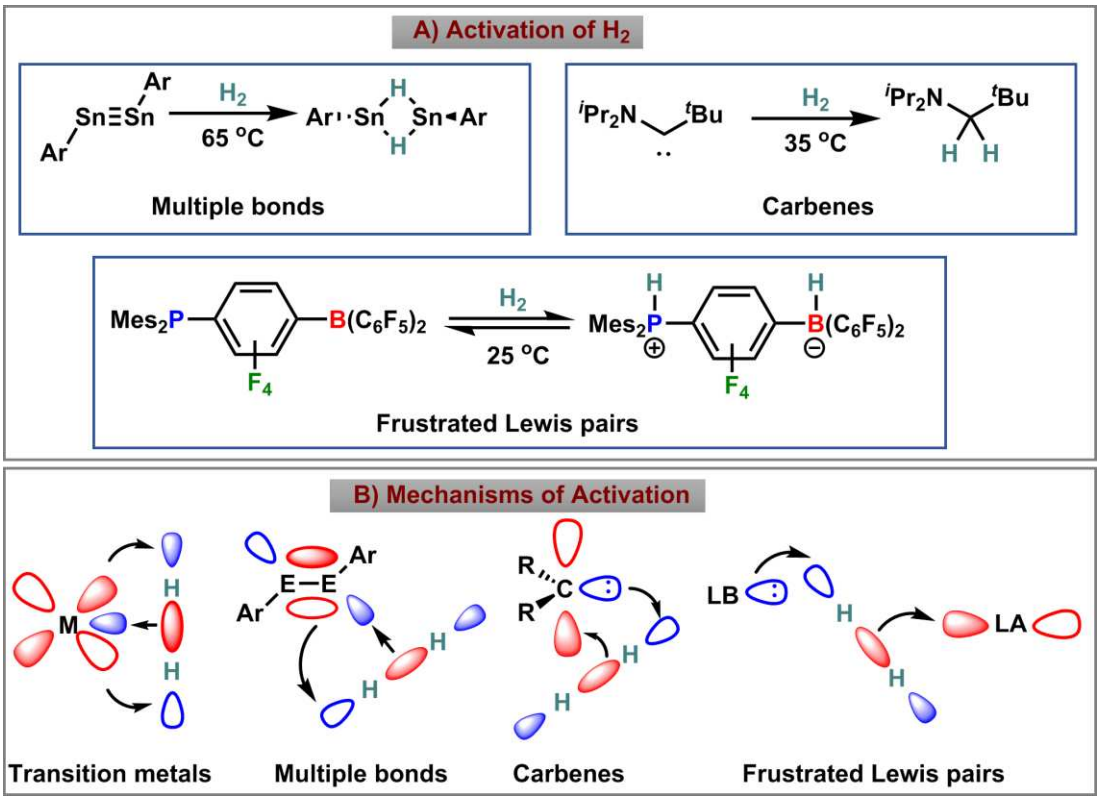

Fig. 2. Dihydrogen activation. (**A**) Activation of dihydrogen with *p*-block elements (Ar = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$). (**B**) Mechanisms of activation.

Reactions of *p*-block elements with CO_2 have garnered attention. Activation of CO_2 has been achieved using both multiple bonded compounds and FLPs.(*1*,*2*,*34*) In the latter systems, activation of CO_2 proceeds through a cooperative action of the Lewis base at carbon and the Lewis acid at an oxygen atom.(*40*) Through judicious choice of the Lewis acid and base, hydrogenation of the CO_2 bound intermediate affords CH_3OH.(*42*) As with FLPs, heteronuclear E=E′ bonds also react with CO_2 owing to differences in electronegativity of the elements and polarity of the double

bond.(*1*) Conversely, the corresponding reactions of homonuclear E=E bonds are much rarer. However, aromatic diazadiborinine compounds have been shown to undergo [4+2] additions with CO_2, and a boron–boron double bond was found to react with CO_2 through an initial [2+2] cycloaddition.(*43*,*44*)

Reactions of *p*-block elements such as selenium, iodine, and boron with C-C π-bonds have received much attention for applications in organic synthesis. However, reactions with gaseous ethane and ethylene are much less studied, yet multiple bonds of aluminum and tin have been shown to react with alkenes yielding formal [2+2] addition products.(*2*,*45*,*46*) Another application that exploits the reactions of *p*-block elements with C-C π-bonds is in gas separation. The separation of saturated and unsaturated hydrocarbons is critical to industries such as petroleum refining. FLPs are unreactive with alkanes but undergo addition to alkenes. Using segmented gas–liquid microfluidic flow, the ^{t}Bu$_3$P/B(C$_6$F$_5$)$_3$ FLP was shown to be an efficient reagent to separate ethylene and ethane mixtures (Fig. 3A). This work may pave the way to effective methods to separate gases provided routes to subsequently release the ethylene and to recycle the FLP can be found.(*47*)

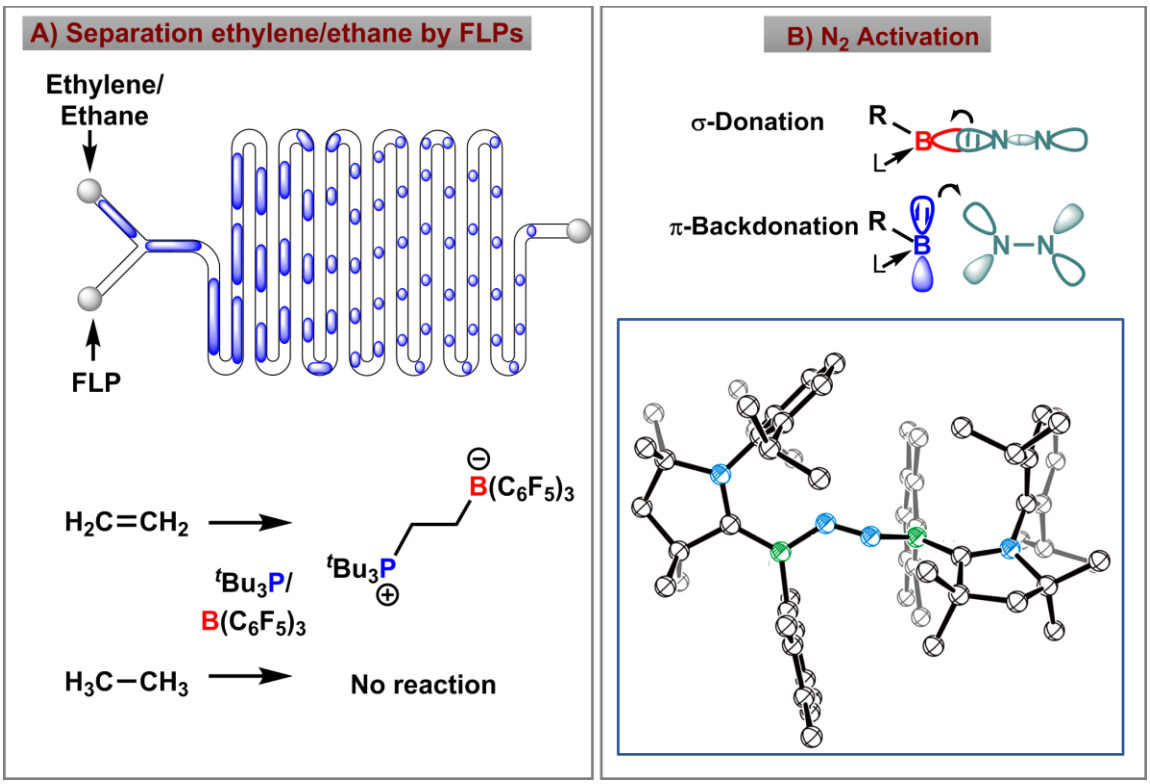

Fig. 3. **Small molecule activation.** (**A**) Separation of ethylene and ethane using FLPs. (**B**) Activation of N_2 using borylenes through bonding and back-bonding interactions and the N_2 activated complex (crystal structure).

Of all the small molecules, N_2 is one of the most difficult to activate. Even for transition metals this still represents a substantial challenge. The Haber–Bosch process has been known for over a century, and although the process is energy intensive, viable alternatives remain elusive. Very recently, *p*-block elements have been shown to assist *d*-block elements in the activation and functionalization of N_2. Specifically, the strong Lewis acid B(C$_6$F$_5$)$_3$ has been shown to weaken

the N–N bond in M-N_2 (M = Fe, Mo, W) complexes to allow for subsequent reaction through protonation, hydroboration or hydrosilylation of the N_2 unit.(*48*,*49*) In a truly seminal finding, the CAAC stabilized borylene [(CAAC)BDur] (Dur = 2,3,5,6-tetramethylphenyl) was very recently found to activate N_2 in the absence of transition metals (Fig. 3B).(*50*) The product displays a significantly elongated N-N bond as the two boron centers act in a "push-pull" fashion to weaken the N≡N bond. This discovery represents an exciting leap forward in the chemistry of the *p*-block. It is likely that in the future other *p*-block systems will be targeted for N_2 activation and conversion.

Catalysis

The development of novel catalysts and improvements in catalytic performance have a direct influence on society and play a pivotal role in maintaining the quality of life. The *d*-block elements have dominated catalytic processes; however, many catalysts rely on scarce, often toxic utilize "precious" metals.(*51*) This prompts interest in the potential of *p*-block catalysts to replace metals, reducing purification costs and lowering toxicity, while at the same time offering unique selectivity or reactivity. Organocatalysis is now well-established(*52*) but, with the exception of simple Lewis acid catalysis (using e.g. $AlCl_3$), the use of other *p*-block elements in homogenous catalysis is a more recent area of exploration. The small molecule activation studies described earlier were crucial in the realization that catalytic processes could be developed with *p*-block elements. Importantly, the studies that demonstrated the use of a perfluorinated aryl borane catalyst in hydrosilylation foreshadowed the broader use of *p*-block elements in catalysis.(*53*) Indeed, the advent of FLP activation of hydrogen prompted metal-free hydrogenation catalysis. In the first study, the intramolecular FLPs $(R_2P)C_6F_4(B(C_6F_5)_2)$ (R = Mes, ^{t}Bu) were found to catalyze the reduction of imines to amines (Fig. 4A).(*54*) This study led to a range of FLPs being developed and applied in metal-free hydrogenation of a variety of substrates. Key developments in this regard include the FLP-catalyzed hydrogenation of ketones using ethereal solvents as the Lewis base(*55*,*56*) as well as the use of FLPs to catalyze the highly chemo- and stereo-selective hydrogenation alkynes to *cis*-alkenes.(*57*) For applications in organic synthesis, chiral FLP catalysts have been targeted for application to asymmetric reductions. For example, chiral bis-boranes(*58*) and chiral aminoborane(*59*) catalysts have been found to give enantioselectivities of up to 90% in the FLP reduction of prochiral imines. In addition to hydrogenation catalysis, FLPs have also proven effective in C-H dehydrogenative borylation of heteroarenes,*(60*) a reaction typically performed by transition metals.(*24*)

Of particular interest have been catalytic methods to transform CO_2 into useful hydrocarbons using *p*-block elements. Whereas most reported systems are typically heterogeneous metal-based catalysts, the stoichiometric fixation of CO_2 by FLPs suggests their potential in the catalytic reduction of CO_2. The *o*-phenylene bridged catalyst 1-BCat-2-PPh_2-C_6H_4 was capable of catalyzing the hydroboration of CO_2 to methoxy boranes with excellent turnover frequencies and turnover numbers (Fig. 4B).(*61*) The catalytic *N*-formylation of amines with CO_2 has also been achieved in a metal-free manner to yield synthetically useful formamides via an aromatic diazadiborinine catalyst (Fig. 4B).(*62*)

In the search for other *p*-block Lewis acid catalysts, the salt $[(C_6F_5)_3PF][B(C_6F_5)_4]$ was developed.(*63*) The cation was found to have an extremely high Lewis acidity owing to the four electron withdrawing substituents resulting in a low lying P-F σ*-orbital. This high electrophilicity of the cation enables activation of C(sp^3)–F bonds. Approaches to degrade fluorocarbons or to functionalize C-F bonds are generally challenged by the high dissociation energy. In addition to

other reactions, this phosphonium catalyst has been found to catalyze hydrodefluorination reactions as well as hetero-dehydrocoupling reactions between *p*-block E-H and E'-H bonds (E = O, N, S; E' = Si) (Fig. 4C).(*64*)

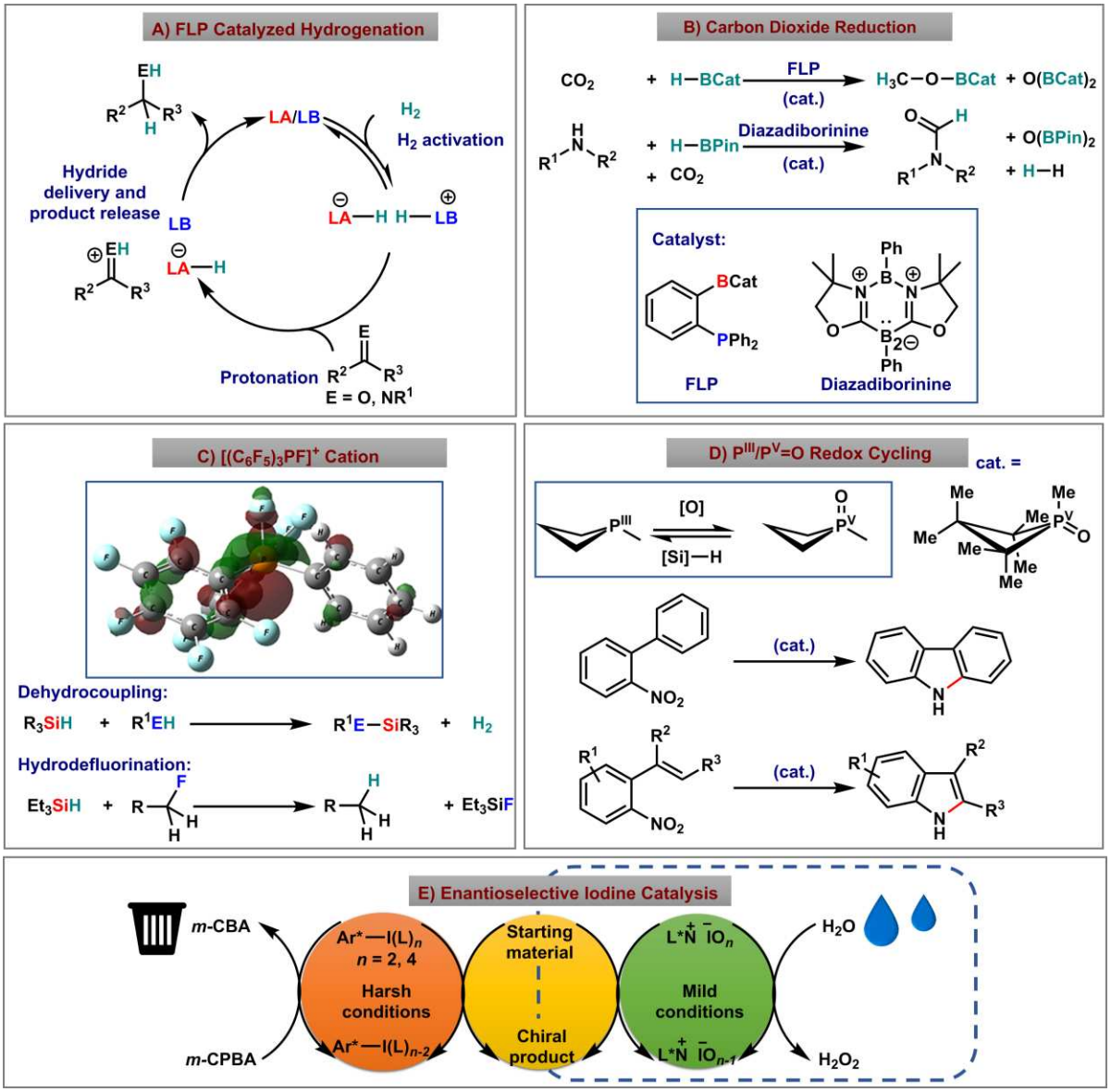

Fig. 4. *p*-Block catalysis. (**A**) FLP catalyzed hydrogenation of imines and alkynes. (**B**) Catalytic CO_2 reduction. (**C**) Phosphonium catalysis. (**D**) P^{III}/P^{V} redox cycling. (**E**) Stereoselective hypervalent iodine catalysis.

In contrast to metal-based catalysis, catalytic reactions using *p*-block elements do not generally involve a change in oxidation state. For instance, phosphorus(III) compounds have been used in C-C coupling reactions reminiscent of that in Pd catalyzed process which involves a phosphorus(V) intermediate.(*65*) This reaction however is stoichiometric as the starting phosphine cannot be regenerated. Nonetheless, catalytic systems based upon a P^{III}/P^{V} redox couple have been developed and employed in catalysis.(*66*) Similarly, behaving as biphilic reagents, small-ring phosphacycles (phosphetanes) have been shown to be active in P^{III}/P^{V}=O redox cycling in oxygen

atom-transfer catalysts. The 4-membered, 1,2,2,3,4,4-hexamethylphosphetane P-oxide was found to be an excellent catalyst for N−N bond-forming heterocyclization reactions in the Cadogan indazole synthesis,(*67*) and for intramolecular C−N heterocyclization of *o*-nitrobiaryl and -styrenyl compounds to access carbazole and indole products (Fig. 4D).(*68*)

Although hypervalent iodine compounds have long been applied in organic synthesis, these compounds are typically used in stoichiometric quantities.(*69*) Nevertheless, examples of catalytic reactions are emerging with the use of stoichiometric oxidants to regenerate the hypervalent iodine reagent (Fig. 4E). The choice of oxidant in these reactions is crucial since the oxidant must selectively oxidize the iodine species and not the substrate. For example, *meta*-chloroperbenzoic acid (*m*CPBA) can be used as oxidant to regenerate hypervalent iodine(III) reagents for the spirocyclization of phenol derivatives. Using this method only 5 mol% of iodotoluene is needed to generate the lactone products.(*70*) Similar conditions have been used to enable the α-oxygenation of carbonyl compounds using a catalytic amount of an iodoarene with *m*CPBA as the oxidant.(*71*) An improvement to this reaction, which frequently relies on harsh conditions and generates *meta*-chlorobenzoic acid (*m*CBA) waste, was later reported whereby the oxidative coupling reactions of carbonyl compounds with carboxylic acids could be achieved using catalytic amounts of *tetra*-butylammonium (hypo)iodite and an environmentally benign oxidant (either hydrogen peroxide or *tert*-butyl hydroperoxide).(*72*) Hydrogen peroxide was also used as the oxidant to oxidize chiral quaternary ammonium iodide salts *in situ* to yield the active (hypo)iodite which could be employed as a catalyst for the asymmetric oxidative cycloetherification of ketophenols to yield biologically relevant 2-acyl-2,3-dihydrobenzofuran derivatives (Fig. 4E).(*73*)

Outlook

It is clear from this short review that the renaissance of main group chemistry is accelerating as fundamentally new principles and reactivity continue to emerge with our developing understanding of the diverse reactivity of the *p*-block. Moreover *p*-block chemists will glean some insights from the broad base of knowledge surrounding transition metal chemistry to design and find new applications in synthetic chemistry. While *p*-block catalysts, will undoubtedly present their own challenges, the promise of new reactivity and the potential for commercial applications keep the chemistry of the *p*-block elements perpetually exciting.

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